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RUBBER COMPOSITION AND PNEUMATIC TIRE

Abstract:

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(71) Applicant:

BRIDGESTONE CORPORATION
Tokyo 104-0031 (JP)

(72) Inventors:

- HOJO, Masahiro
Kodaira-shi, Tokyo 187-0031 (JP)
- AJIRO, Yukitoshi
Kodaira-shi, Tokyo 187-0031 (JP)
- FUJINO, Kentaro
Kodaira-shi, Tokyo 187-0031 (JP)
- BABA, Shunji
Kodaira-shi, Tokyo 187-0031 (JP)

(74) Representative:

Lamb, Martin John Carstairs
MARKS & CLERK,
57-60 Lincoln's Inn Fields
London WC2A 3LS (GB)

(54) RUBBER COMPOSITION AND PNEUMATIC TIRE

(57) There are provided a rubber composition having a high modulus of elasticity and a good workability, and a pneumatic tire.

A rubber composition comprising at least one of natural rubber and synthetic diene rubbers as a rubber ingredient, at least one maleimide compound, and at least one nitrogen-containing compound selected from the group consisting of polyaniline, hydrazide, and amine compound is used in a tread.

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Description

[Technical Field of the Invention]

5 [0001] This invention relates to a rubber composition and a pneumatic tire, and more particularly to a technique for obtaining a rubber composition having a good workability and a high modulus of elasticity as well as a pneumatic tire.

[Prior Art]

10 [0002] Recently, it is demanded to develop the steering stability and gripping property higher than the conventional one even in tire performances as power and running speed of automobiles become higher.

[0003] In rubber industry, bismaleimide is practically examined as a cross-linking agent. In JP-A-63-99251 is reported that the heat resistance and the high maneuverability are simultaneously established by compounding a bismaleimide compound with a styrene-butadiene copolymer rubber (SBR). And also, the effect of lowering heat build-up through hydrazide as reported in JP-A-10-139934.

15 [0004] Among various road surface conditions, a wet road surface on a rainy day is slippery, so that the running of automobiles is risky. And also, there is recently a tendency to take a regulation to a braking distance and hence wet-skid performances become increasingly important.

[0005] As a conventional technique for improving wet-skid performances, there are a method of shifting T_g of a polymer to a higher temperature side to increase $\tan \delta$ (0°C), a method of compounding silica to improve wet performances, and so on.

[0006] However, in the former method of increasing $\tan \delta$, it is difficult to simultaneously establish other performances such as dry-skid performances, low rolling resistance and the like. And also, in the latter method of compounding silica, there are disadvantages that a lock μ at wet state (frictional coefficient when a tire is fully locked and slipping 100 %)

25 [0007] On the other hand, the applicant has discovered that the wet-skid performances can be improved by using N,N'-(1,3-phenylene)bismaleimide and silica together. However, it has been confirmed that when compounding N,N'-(1,3-phenylene)bismaleimide, $\tan \delta$ at 60°C is not sufficiently lowered, and the rolling resistance becomes slightly high when being used in a tire tread.

[Problems to be solved by the Invention]

30 [0008] Recently, the inventors have discovered that when bismaleimide is compounded with rubber containing not less than 50% by weight of SBR together with silica, not only a heat resistance is improved but also a dynamic storage modulus (E') becomes higher and the steering stability is improved when such a rubber composition using bismaleimide is used in a tread.

[0009] However, when a greater amount of bismaleimide is compounded with SBR-containing rubber as mentioned above, vulcanization reaction is obstructed by bismaleimide and hence a long time is taken in the vulcanization and also a blow point (easiness of bubble generation in rubber) at the same vulcanizing degree becomes higher, so that it is necessary to take further longer vulcanization time in order to conduct the vulcanization without leaving bubbles in a rubber article, and the productivity largely lowers and becomes impracticable.

40 [0010] As regards this problem, it can naturally be considered to use an accelerator quickening the start-up of the vulcanization or so-called ultra-accelerator such as guanidines, dithiocarbamates and xanthates. However, these compounds can quicken the start-up of vulcanization to shorten a burning time (scorch time) of an uncured rubber, but fail to largely improve the blow point.

[0011] Therefore, the inventors have investigated a cause of obstructing the vulcanization reaction through bismaleimide and confirmed that a reaction between a vulcanization accelerator and a bismaleimide occurs earlier than the vulcanization reaction particularly in SBR compounded system and hence the vulcanization is obstructed are used. This is particularly more remarkable when thiazole-based and thiuram-based vulcanization accelerators are used. Further, it has been confirmed that a part of bismaleimide is decomposed and gasified due to the reaction between a bismaleimide and a vulcanization accelerator and hence an amount of gas larger than in a usual case is generated in rubber to degrade the blow point.

50 [0012] It is, therefore, an object of the invention to solve the above problems and to provide a technique capable of further improving a merit of bismaleimide for the increase in elasticity and avoiding a demerit of productivity due to the delay in vulcanization and to provide a rubber composition capable of providing a pneumatic tire with a remarkable non-slip effect, excellent wet-skid performances and a low rolling resistance on a wet road surface having an extremely low frictional coefficient.

[Means for solving the Problems]

[0013] In order to achieve the above object, the invention is constituted as follows.

[0014] The rubber composition according to the invention is characterized by comprising at least one rubber of natural rubber and synthetic diene rubbers as a rubber ingredient, at least one maleimide compound, and at least one nitrogen-containing compound selected from the group consisting of polyanilines, hydrazides and amine compounds. And also, the rubber composition is characterized by comprising at least one rubber of natural rubber and synthetic diene rubbers and at least one maleimide compound selected from the group consisting of bismaleimide, oligomers and polymers of bismaleimide.

[0015] Further, the pneumatic tire according to the invention uses the above rubber composition in its tread.

[Embodiments of the Invention]

[0016] The invention will be described in detail below.

[0017] In the invention can be used natural rubber and synthetic diene rubbers. As the synthetic diene rubber, mention may be made of cis-1,4-polyisoprene, styrene-butadiene copolymer, polybutadiene, low cis-1,4-polybutadiene, high cis-1,4-polybutadiene, ethylene-propylene-diene terpolymer, chloroprene, halogenated butyl rubber, acrylonitrile-butadiene rubber and so on. The natural rubber and synthetic diene rubbers may be used alone or in a blend thereof.

[0018] The natural rubber and at least one of cis-1,4-polyisoprene, styrene-butadiene copolymer and polybutadiene as the diene rubber are preferable because the improving effect by the combination with bismaleimide and hydrazide aiming at the invention is made clear.

[0019] And also, it is preferable that the remarkable effect is obtained when at least one of butadiene rubber (BR) and styrene-butadiene copolymer rubber (SBR) is included in the rubber ingredient in an amount of not less than 50% by weight. More preferably, the amount is not less than 80% by weight.

[0020] Heretofore, a maleimide compound is applied to a rubber composition containing, for example, natural rubber or isoprene rubber in an amount of not less than 50% by weight of the rubber ingredient. In this case, however, the tensile stress of full region becomes too high due to the compounding of maleimide and the object of the invention can not sufficiently be attained. And also, when butyl rubber is included in an amount of not less than 50% by weight, the increase of tensile stress in a desired region becomes small even in the compounding of the maleimide, so that the object of the invention can not be attained sufficiently likewise the above case.

[0021] Comparing BR and SBR with each other, SBR is preferable from a viewpoint of the establishment with the gripping performance, and further the use of an emulsion polymerized SBR is preferable in view of wear resistance.

[0022] As the maleimide compounds used in the invention, a bismaleimide compound represented by the formula [7], or an oligomer or polymer of bismaleimide is preferable.

[0023] Moreover, when R^{19} or R^{20} in the general formula [7] of the bismaleimide compound is an alkylene group, if the carbon number is not less than 4, the molecular weight of the bismaleimide compound becomes large, so that the increasing effect of dynamic storage modulus aimed at the invention is not obtained at the compounding amount thereof.

[0024] As the bismaleimide compounds preferably usable in the invention, mention may be made of N,N'-(1,2-phenylene) bismaleimide, N,N'-(1,3-phenylene) bismaleimide, N,N'-(1,4-phenylene) bismaleimide, N,N'-(4,4'-diphenylmethane) bismaleimide, 2,2-bis[4-(4-maleimidophenoxy)phenyl] propane, bis(3-ethyl,5-methyl-4-maleimidophenyl)methane and so on. One or more of them may be included in the rubber composition.

[0025] As the oligomer or polymer of bismaleimide preferably usable in the invention, mention may be made of (1) polybismaleimide oligomer or polymer obtained by simply oligomerizing or polymerizing bismaleimide, (2) polyaminobismaleimide oligomer or polymer obtained from bismaleimide and diamine, (3) bismaleimide triazine oligomer or polymer obtained from bismaleimide and dicyanate and so on.

[0026] And also, the maleimides as a starting material for bismaleimide oligomer or polymer may include N,N'-(1,2-phenylene)bismaleimide, N,N'-(1,3-phenylene)bismaleimide, N,N'-(1,4-phenylene)bismaleimide, 1,1'-(methylenedi-4,1-phenylene)bismaleimide and so on. One or more of them can be included.

[0027] Furthermore, the diamines as a starting material for polyaminobismaleimide oligomer or polymer may include p-phenylenediamine, m-phenylenediamine, bis(4-aminophenyl) methane, bis(4-aminophenyl) ether, bis(4-aminophenyl) sulphone, bis(4-aminophenyl) sulfide and so on. One or more of them can be included.

[0028] Moreover, the triazines as a starting material for the bismaleimide triazine oligomer or polymer or a starting material thereof may include cyanuric acid, monocyanate, dicyanate and so on.

[0029] In the invention, the oligomer or polymer of bismaleimide is favorable to have a softening point of not higher than 120°C. This is due to the fact that when the softening point exceeds 120°C, it tends to degrade the fracture properties of the rubber composition.

[0030] In the invention, the compounding amount of the maleimide compound is preferable to be 0.1-30 parts by

weight per 100 parts by weight of the rubber ingredient. When it is less than 0.1 part by weight, the effect by the compounding may not sufficiently be obtained, while when it exceeds 30 parts by weight, it tends to degrade the fracture properties. From the similar viewpoint, the amount is preferably 0.5-10 parts by weight, more preferably 0.5-5.0 parts by weight, more particularly 0.5-3.0 parts by weight.

[0031] Particularly, in case of using N,N'-(4,4-diphenylmethane) bismaleimide, the compounding amount is preferable to be 0.5-4 parts by weight per 100 parts by weight of the rubber ingredient. When it is less than 0.5 part by weight, the improving effect of wet performances is not sufficient, while when it exceeds 4 parts by weight, the hardening of rubber tends to become severe and the cost becomes expensive.

[0032] The polyanilines preferably used in the invention includes bisanilines, aromatic polyanilines and the like. As the bisanilines, mention may be made of p-phenylenediamine, m-phenylenediamine, bis(4-aminophenyl) methane, bis(4-aminophenyl) ether, bis(3-aminophenyl) sulphone, bis(4-aminophenyl) sulphone, bis(4-aminophenyl) sulfide, 4,4'-(m-phenylene diisopropylidene) dianiline and so on. The aromatic polyanilines may include aromatic polyanilines represented by the general formula [1] and so on. One or more of them may be included in the rubber composition.

[0033] Moreover, when n is 0 or 1 in the polyanilines represented by the formula [1], the modulus of elasticity is not sufficiently improved. And also, the carbon number of R⁶ is not particularly limited. Further, the possible range of 1 in the aromatic polyanilines represented by the formula [2] is an integer of 0 or more, preferably an integer of 0-80.

[0034] Further, the compounding amount of the polyanilines is preferable to be 10-200% by weight of the maleimide compound. When the amount is less than 10% by weight, the synergistic effect by the combination with the maleimide compound is not sufficiently obtained, while when it exceeds 200% by weight, the vulcanization is promoted and the rubber tends to be scorched. From the similar viewpoint, the amount is preferably 20-100% by weight.

[0035] As a compound represented by the formula [3] among hydrazides used in the invention, mention may be made of 1-hydroxy, N'-(1-methylethylidene)-2-naphthoic acid hydrazide, 1-hydroxy, N'-(1-methylpropylidene)-2-naphthoic acid hydrazide, 1-hydroxy, N'-(1-methylbutylidene)-2-naphthoic acid hydrazide, 1-hydroxy, N'-(1,3-dimethylbutylidene)-2-naphthoic acid hydrazide, 1-hydroxy, N'-(2,6-dimethyl-4-heptylidene)-2-naphthoic acid hydrazide, 1-hydroxy, N'-(2-furylmethylene)-2-naphthoic acid hydrazide, 3-hydroxy, N'-(1-methylethylidene)-2-naphthoic acid hydrazide, 3-hydroxy, N'-(1-methylpropylidene)-2-naphthoic acid hydrazide, 3-hydroxy, N'-(1-methylbutylidene)-2-naphthoic acid hydrazide, 3-hydroxy, N'-(1,3-dimethylbutylidene)-2-naphthoic acid hydrazide, 2-hydroxy, N'-(2-furylmethylene)-3-naphthoic acid hydrazide, isophthalic acid di(1-methylethylidene) hydrazide, isophthalic acid di(1-methylpropylidene) hydrazide, isophthalic acid di(1-methylbutylidene) hydrazide, isophthalic acid di(1,3-dimethylbutylidene) hydrazide, isophthalic acid di(2,6-dimethyl-4-heptylidene) hydrazide, isophthalic acid di(2-furylmethylene) hydrazide, isonicotinic acid (1-methylethylidene) hydrazide, isonicotinic acid (1-methylpropylidene) hydrazide, isonicotinic acid (1-methylbutylidene) hydrazide, isonicotinic acid (2,6-dimethyl-4-heptylidene) hydrazide, isonicotinic acid (1,3-dimethylbutylidene) hydrazide, isonicotinic acid (2-furylmethylene) hydrazide, N'-(1-methylethylidene)-salicylic acid hydrazide, N'-(1-methylpropylidene)-salicylic acid hydrazide, N'-(1-methylbutylidene)-salicylic acid hydrazide, N'-(1,3-dimethylbutylidene)-salicylic acid hydrazide, N'-(2,6-dimethyl-4-heptylidene)-salicylic acid hydrazide, N'-(2-furylmethylene)-salicylic acid hydrazide, N'-(1-methylethylidene)-benzoic acid hydrazide, N'-(1-methylpropylidene)-benzoic acid hydrazide, N'-(1,3-dimethylbutylidene)-benzoic acid hydrazide, N'-(benzylidene)-benzoic acid hydrazide, N'-(4-dimethylaminophenylmethylene)-benzoic acid hydrazide, N'-(4-methoxyphenylmethylene)-benzoic acid hydrazide, N'-(4-hydroxyphenylmethylene)-benzoic acid hydrazide, N'-(1-phenylethylidene)-benzoic acid hydrazide, N'-(diphenylmethylene)-benzoic acid hydrazide, N'-[1-(2,4-dihydroxyphenyl) benzylidene]-benzoic acid hydrazide, N'-(2-furylmethylene)-benzoic acid hydrazide, N'-(1-methylethylidene)-1-naphthoic acid hydrazide, N'-(1-methylpropylidene)-1-naphthoic acid hydrazide, N'-(1,3-dimethylbutylidene)-1-naphthoic acid hydrazide, N'-(benzylidene)-1-naphthoic acid hydrazide, N'-(4-dimethylaminophenylmethylene)-1-naphthoic acid hydrazide, N'-(4-methoxyphenylmethylene)-1-naphthoic acid hydrazide, N'-(4-hydroxyphenylmethylene)-1-naphthoic acid hydrazide, N'-(1-phenylethylidene)-1-naphthoic acid hydrazide, N'-(diphenylmethylene)-1-naphthoic acid hydrazide, N'-(1-(2,4-dihydroxyphenyl) benzylidene)-1-naphthoic acid hydrazide, N'-(2-furylmethylene)-1-naphthoic acid hydrazide, N'-(1-methylpropylidene)-2-naphthoic acid hydrazide, N'-(benzylidene)-2-naphthoic acid hydrazide, N'-(4-dimethylaminophenylmethylene)-2-naphthoic acid hydrazide, N'-(4-methoxyphenylmethylene)-2-naphthoic acid hydrazide, N'-(4-hydroxyphenylmethylene)-2-naphthoic acid hydrazide, N'-(1-phenylethylidene)-2-naphthoic acid hydrazide, N'-(diphenylmethylene)-2-naphthoic acid hydrazide, N'-[1-(2,4-dihydroxyphenyl) benzylidene]-2-naphthoic acid hydrazide, N'-(2-furylmethylene)-2-naphthoic acid hydrazide, N'-(1-methylethylidene)-propionic acid hydrazide, N'-(1-methylpropylidene) propionic acid hydrazide, N'-(1,3-dimethylbutylidene)-propionic acid hydrazide, N'-(benzylidene) propionic acid hydrazide, N'-(4-dimethylaminophenylmethylene)-propionic acid hydrazide, N'-(4-methoxyphenylmethylene) propionic acid hydrazide, N'-(4-hydroxyphenylmethylene)-propionic acid hydrazide, N'-(1-phenylethylidene)-propionic acid hydrazide, N'-(diphenylmethylene)-propionic acid hydrazide, N'-[1-(2,4-dihydroxyphenyl) benzylidene]-propionic acid hydrazide, N'-(2-furylmethylene)-propionic acid hydrazide, N'-(1-methylethylidene)-2-methyl-propionic acid hydrazide, N'-(1-methylpropylidene)-2-methyl-propionic acid hydrazide, N'-(1,3-dimethylbutylidene)-2-methyl-pro-

pionic acid hydrazide, N'-(benzylidene), 2-methyl-propionic acid hydrazide, N'-(4-dimethylaminophenylmethylene), 2-methyl-propionic acid hydrazide, N'-(4-methoxyphenylmethylene), 2-methyl-propionic acid hydrazide, N'-(4-hydroxyphenylmethylene), 2-methyl-propionic acid hydrazide, N'-(1-phenylethylidene), 2-methyl-propionic acid hydrazide, N'-(diphenylmethylene), 2-methyl-propionic acid hydrazide, N'-[1-(2,4-dihydroxyphenyl) benzylidene], 2-methyl-propionic acid hydrazide, N'-(2-furylmethylene), 2-methyl-propionic acid hydrazide, N'-(1-methylethylidene), 2,2-dimethyl-propionic acid hydrazide, N'-(1-methylpropylidene), 2,2-dimethyl-propionic acid hydrazide, N'-(1,3-dimethylbutylidene), 2,2-dimethyl propionic acid hydrazide, N'-(benzylidene), 2,2-dimethyl-propionic acid hydrazide, N'-(4-dimethylaminophenylmethylene), 2,2-dimethyl-propionic acid hydrazide, N'-(4-methoxyphenylmethylene), 2,2-dimethyl-propionic acid hydrazide, N'-(4-hydroxyphenylmethylene), 2,2-dimethyl-propionic acid hydrazide, N'-(1-phenylethylidene), 2,2-dimethyl-propionic acid hydrazide, N'-(diphenylmethylene), 2,2-dimethyl-propionic acid hydrazide, N'-[1-(2,4-dihydroxyphenyl) benzylidene], 2,2-dimethyl propionic acid hydrazide, N'-(2-furylmethylene), 2,2-dimethyl-propionic acid hydrazide and so on. One or more of them can be included in the rubber composition.

[0036] As a preferable hydrazide among them, there are 1-hydroxy, N'-(1-methylethylidene)-2-naphthoic acid hydrazide, 1-hydroxy, N'-(1-methylpropylidene)-2-naphthoic acid hydrazide, 1-hydroxy, N'-(1-methylbutylidene)-2-naphthoic acid hydrazide, 1-hydroxy, N'-(1,3-dimethylbutylidene)-2-naphthoic acid hydrazide, 1-hydroxy, N'-(2,6-dimethyl-4-heptylidene)-2-naphthoic acid hydrazide, 1-hydroxy-N'-(2-furylmethylene)-2-naphthoic acid hydrazide, 3-hydroxy, N'-(1-methylethylidene)-2-naphthoic acid hydrazide, 3-hydroxy, N'-(1-methylpropylidene)-2-naphthoic acid hydrazide, 3-hydroxy, N'-(1-methylbutylidene)-2-naphthoic acid hydrazide, 3-hydroxy, N'-(1,3-dimethylbutylidene)-2-naphthoic acid hydrazide, 2-hydroxy, N'-(2,6-dimethyl-4-heptylidene)-3-naphthoic acid hydrazide, 2-hydroxy, N'-(2-furylmethylene)-3-naphthoic acid hydrazide, isophthalic acid-di(1-methylethylidene) hydrazide, isophthalic acid-di(1-methylpropylidene) hydrazide, isophthalic acid-di(1-methylbutylidene) hydrazide, isophthalic acid-di(1,3-dimethylbutylidene) hydrazide, isophthalic acid-di(2,6-dimethyl-4-heptylidene) hydrazide, isophthalic acid-di(2-furylmethylene) hydrazide, isonicotinic acid-(1-methylethylidene) hydrazide, isonicotinic acid-(1-methylpropylidene) hydrazide, isonicotinic acid-(1-methylbutylidene) hydrazide, isonicotinic acid-(2,6-dimethyl-4-heptylidene) hydrazide, isonicotinic acid-(1,3-dimethylbutylidene) hydrazide, isonicotinic acid-(2-furylmethylene) hydrazide, N'-(1-methylethylidene)-salicylic acid hydrazide, N'-(1-methylpropylidene)-salicylic acid hydrazide, N'-(1-methylbutylidene)-salicylic acid hydrazide, N'-(1,3-dimethylbutylidene)-salicylic acid hydrazide, N'-(2,6-dimethyl-4-heptylidene)-salicylic acid hydrazide and N'-(2-furylmethylene)-salicylic acid hydrazide.

[0037] Moreover, when s in the formula [3] is not less than 4, the molecular weight of hydrazide becomes large and it is undesirably required to largely increase the compounding amount. When R¹ is outside the definition, the given effect is not sufficiently obtained.

[0038] As a compound represented by the formula [4] among the hydrazides used in the invention, mention may be made of semicarbazide, carbohydrazide, oxalic acid dihydrazide, malonic acid dihydrazide, succinic acid dihydrazide, glutaric acid dihydrazide, adipic acid dihydrazide, pimelic acid dihydrazide, suberic acid dihydrazide, azelaic acid dihydrazide, sebacic acid dihydrazide, 1,12-dodecane dicarboxylic acid dihydrazide, 1,16-hexadecane dicarboxylic acid dihydrazide, terephthalic acid dihydrazide, isophthalic acid dihydrazide, 2,6-naphthoic acid dihydrazide, 1,4-naphthoic acid dihydrazide, 2,6-pyridine dihydrazide, 4,4'-bisbenzene dihydrazide, salicylic acid hydrazide, p-hydroxy benzoic acid hydrazide, 1-hydroxy-2-naphthoic acid hydrazide, 2-hydroxy-3-naphthoic acid hydrazide, aminobenzoic acid hydrazide and so on. Among them, adipic acid dihydrazide, isophthalic acid dihydrazide, salicylic acid hydrazide and 2-hydroxy-3-naphthoic acid hydrazide are preferable. One or more of them can be included in the rubber composition.

[0039] Even in case of the formula [4] likewise the formula [3], when s is not less than 4, the molecular weight of hydrazide becomes large and it is undesirably required to largely increase the compounding amount, and when R¹ is outside the definition, the given effect is not sufficiently obtained.

[0040] Moreover, the compounding amount of hydrazide is preferable to be 5-200% by weight of the compounding amount of the maleimide compound. When the amount is less than 5% by weight, the synergistic effect by the combination with the maleimide compound is not obtained, while when it exceeds 200% by weight, vulcanization is promoted and the rubber tends to be scorched. From the similar viewpoint, the amount is preferably 10-100% by weight.

[0041] The amine compound used in the invention is as follows.

[0042] The specified alkyl group adoptable as R¹ in the formulae [5 and 6] for the amine and amine addition salt may be straight, branched or cyclic, and includes various octyl groups, various nonyl groups, various decyl groups, various dodecyl groups, various tetradecyl groups, various hexadecyl groups, various octadecyl groups, various behenyl groups, various octenyl groups, various decenyl groups, oleyl group, cyclooctyl group, cyclododecyl group, various cyclooctenyl groups, various cyclododecenyl groups and so on.

[0043] The specified aryl group adoptable as R¹³ in the formulae [5 and 6] may have an adequate substituent such as straight, branched or cyclic lower alkyl group or the like on the aromatic ring, and includes phenyl group, various tolyl groups, various xylyl groups, α - or β -naphthyl group, various methylnaphthyl groups, various dimethylnaphthyl groups and so on.

[0044] The specified aralkyl group adoptable as R¹³ in the formulae [5 and 6] may have an adequate substituent

such as straight, branched or cyclic lower alkyl group or the like on the aromatic ring, and includes benzyl group, various methylbenzyl groups, phenethyl group, various methylphenethyl groups, various naphthylmethyl groups, various (methylnaphthyl)methyl groups and so on.

[0045] The specified alkyl group adoptable as R^{14} and R^{15} in the formulae [5 and 6] may be straight, branched or cyclic, and includes methyl group, ethyl group, n-propyl group, isopropyl group, various butyl groups, various pentyl groups, various hexyl groups, various octyl groups, various decyl groups, various dodecyl groups, propenyl group, allyl group, various pentenyl groups, various hexenyl groups, various octenyl groups, various decenyl groups, cyclopentyl group, cyclohexyl group, cyclooctyl group, various cyclopentenyl groups, various cyclohexenyl groups, various cyclooctenyl groups and so on.

[0046] The specified aryl group adoptable as R^{14} and R^{15} in the formulae [5 and 6] may have an adequate substituent such as straight, branched or cyclic lower alkyl group or the like on the aromatic ring, and includes phenyl group, various tolyl groups, various xylyl groups, α - or β -naphthyl group, various methylnaphthyl groups and so on.

[0047] The specified aralkyl group adoptable as R^{14} and R^{15} in the formulae [5 and 6] may have an adequate substituent such as a straight, a branched or a cyclic lower alkyl group or the like on the aromatic ring, and includes benzyl group, various methylbenzyl groups, phenethyl group, various methylphenethyl groups, various naphthylmethyl groups and so on.

[0048] On the other hand, the specified alkyl group adoptable as R^{16} in the formulae [5 and 6] may be straight, branched or cyclic, and includes various hexyl groups, various octyl groups, various nonyl groups, various decyl groups, various dodecyl groups, various tetradecyl groups, various hexadecyl groups, various octadecyl groups, various behenyl groups, various hexenyl groups, various octenyl groups, various decenyl groups, oleyl group, cyclohexyl group, cyclooctyl group, cyclododecyl group, various cyclohexenyl groups, various cyclooctenyl groups, various cyclododecenyl groups and so on.

[0049] The specific aryl group and aralkyl group adoptable as R^{16} in the formulae [5 and 6] may have an adequate substituent such as a straight, a branched or a cyclic lower alkyl group or the like on the aromatic ring, respectively, and may include the same ones as exemplified as the aryl group and aralkyl group in the above description for R^{16} .

[0050] As preferable amines constituting the amine and amine addition salt according to the invention, mention may be made of decylamine, laurylamine, myristylamine, palmitylamine, stearylamine, behenylamine, oleylamine, monomethyl decylamine, monomethyl laurylamine, monomethyl myristylamine, monomethyl palmitylamine, monomethyl stearylamine, monomethyl oleylamine, monoethyl decylamine, monoethyl laurylamine, monoethyl myristylamine, monoethyl palmitylamine, monoethyl stearylamine, monoethyl oleylamine, monopropyl decylamine, monopropyl laurylamine, monopropyl myristylamine, monopropyl palmitylamine, monopropyl stearylamine, monopropyl oleylamine, dimethyl decylamine, dimethyl laurylamine, dimethyl myristylamine, dimethyl palmitylamine, dimethyl stearylamine, dimethyl oleylamine, diethyl decylamine, diethyl laurylamine, diethyl myristylamine, diethyl palmitylamine, diethyl stearylamine, diethyl oleylamine, methylethyl decylamine, methylethyl laurylamine, methylethyl myristylamine, methylethyl palmitylamine, methylethyl stearylamine, methylethyl oleylamine, di(hydroxyethyl) decylamine, di(hydroxyethyl) laurylamine, di(hydroxyethyl) myristylamine, di(hydroxyethyl) palmitylamine, di(hydroxyethyl) stearylamine, di(hydroxyethyl) oleylamine and so on. Among them, tertiary alkyl amines in which each of R^{14} and R^{15} is a saturated or an unsaturated alkyl group having a carbon number of 1-8, respectively, and the total carbon number of R^{13} , R^{14} and R^{15} is 10-24 are particularly favorable.

[0051] On the other hand, as the carboxylic acid constituting the amine addition salt according to the invention, saturated or unsaturated straight chain aliphatic acids in which the carbon number of R^{16} is 10-20 are preferable. As an example of this carboxylic acid, there are mentioned capric acid, lauric acid, myristic acid, palmitic acid, stearic acid, arachic acid, behenic acid, oleic acid and so on.

[0052] The amine addition salt according to the invention is preferable to have a molecular weight of 400-800.

[0053] Moreover, the amine addition salt may contain an inorganic salt such as a phosphate, a phosphite or the like in an amount of about 0.1-10% by weight of the amine addition salt for the purpose of increasing strength of flake or grain to prevent fusion likely caused at a high temperature in summer.

[0054] Further, the compounding amount of the amine compound is preferable to be 50-400% by weight of the maleimide compound. When the amount is less than 50% by weight, the synergistic effect by the combination with the maleimide compound is not obtained, while when it exceeds 400% by weight, vulcanization is promoted and the rubber tends to be scorched. From the similar viewpoint, the amount is preferably 100-200% by weight.

[0055] And also, the vulcanization accelerator usable in the invention is not particularly limited, but is preferably a benzothiazole-based vulcanization accelerator such as MBT (2-mercaptobenzothiazole), DM (dibenzothiazyl disulfide), CBS (N-cyclohexyl-2-benzothiazyl sulfeneamide), TBBS (N-t-butyl-2-benzothiazyl sulfeneamide), TBSI (N-t-butyl-2-benzothiazyl sulfeneimide) or the like; a guanidine-based vulcanization accelerator such as DPG (diphenyl guanidine) or the like; a thiuram-based vulcanization accelerator such as tetraoctyl thiuram disulfide, tetrabenzyl thiuram disulfide, tetramethyl thiuram disulfide, tetrakisobutyl thiuram disulfide or the like; and a dithiocarbamate such as zinc dialkyldithiophosphate, zinc dibenzoyldithiocarbamate or the like. Among them, DM, CBS, TBBS, tetraoctyl thiuram disulfide, and

tetrabenzyl thiuram disulfide are preferable because they exhibit a stable vulcanization system.

[0056] When a vulcanization accelerator such as guanidine type such as DPG (diphenyl guanidine), or zinc dialkyldithiophosphate is used together with the above preferable vulcanization accelerator, it is favorable that the amount of thiazoles, thiurams and dithiocarbamates in the vulcanization accelerator is not less than 50% by weight because the rigidity at a low strain aiming at the invention is enhanced.

[0057] The amount of the vulcanization accelerator used is preferably 0.1-5 parts by weight, more particularly 0.2-3 parts by weight per 100 parts by weight of the rubber ingredient.

[0058] The invention is considerably effective for a rubber composition containing a thiazole based vulcanization accelerator and/or a thiuram based vulcanization accelerator as well as a tire.

[0059] In the invention, at least one of silica, carbon black, calcium carbonate, titanium oxide and the like may be used as a reinforcing filler. Among them, silica and carbon black are preferable.

[0060] The compounding amount of the reinforcing filler is preferably 20-150 parts by weight per 100 parts by weight of the rubber ingredient. When the amount is less than 20 parts by weight, the fracture properties and wear resistance of the vulcanizate are insufficient, while when it exceeds 150 parts by weight, the workability is not favorable.

From the similar viewpoint, it is more preferably 25-80 parts by weight.

[0061] And also, the invention is effective when silica is compounded in an amount of 5-60 parts by weight per 100 parts by weight of the rubber ingredient. When the compounding amount of silica is less than 5 parts by weight, it tends to lower the dry gripping performance, while when it exceeds 60 parts by weight, it tends to degrade the workability.

[0062] As the carbon black used as the reinforcing filler, there are mentioned HAF, ISAF, SAF and so on.

[0063] As silica, precipitated silica is preferably used. Particularly, it has a nitrogen adsorption specific surface area (N_2SA) of 100 to 300 m^2/g , preferably 100 to 250 m^2/g .

[0064] And also, when carbon black and silica are used together, the compounding ratio may arbitrarily be varied in accordance with the compounding purpose.

[0065] In addition to the above rubber ingredient, reinforcing filler, bismaleimide and hydrazide, the rubber composition according to the invention may be compounded with a silane coupling agent, vulcanizing agent, vulcanization accelerator, accelerator activator, antioxidant, antiozonant, age resistor, process oil, zinc white (ZnO), stearic acid and the like, which are usually used in the rubber industry, if necessary.

[0066] As the vulcanizing agent usable in the invention is mentioned, for example, sulfur and the like. The amount used is 0.1-10 parts by weight, preferably 0.5-5.0 parts by weight as a sulfur content per 100 parts by weight of the rubber ingredient. When the amount is less than 0.1 part by weight, the fracture properties and wear resistance of the vulcanized rubber tend to be degraded, while when it exceeds 10 parts by weight, the rubber elasticity tends to be lost.

[0067] In order to ensure an adequate tensile stress, sulfur is compounded in an amount of not less than 1.0 part by weight, more preferably not less than 1.2 parts by weight but not more than 8 parts by weight. When it exceeds 8 parts by weight, there may be problems such that sulfur blooms onto a rubber surface, and the like.

[0068] Furthermore, the compounding amount of the vulcanization accelerator including thiazoles, thiurams and dithiocarbamates is not more than 2 times of the compounding weight of sulfur on the total weight. When the vulcanization accelerator is compounded in excess of this amount, the tensile stress at a large deformation increases and hence the sufficient improvement of wet-skid properties aiming at the invention is not obtained.

[0069] It is also an essential feature of the invention that the crosslinking system is a sulfur crosslinking system with a specific range. For example, the object of the invention can not be attained by crosslinking using an organic peroxide or a resin.

[0070] As the process oil usable in the invention, mention may be made of paraffinic, naphthenic and aromatic ones. The aromatic oils are preferably used in applications regarding the fracture properties and wear resistance as importance, and the naphthenic or paraffinic oils are preferably used in applications regarding the low heat build-up and low temperature properties as importance. The amount used is preferably not more than 100 parts by weight per 100 parts by weight of the rubber ingredient. When it exceeds 100 parts by weight, it tends to degrade the fracture properties and low heat build-up property of the vulcanized rubber.

[0071] A preferable embodiment of the invention is a rubber composition comprising 100 parts by weight of the rubber ingredient, 5-60 parts by weight of silica and 0.5-4 parts by weight of $N,N'-(1,3\text{-phenylene})$ bismaleimide.

[0072] When the compounding amount of $N,N'-(1,3\text{-phenylene})$ bismaleimide is less than 0.5 part by weight, the wet performances are not sufficiently improved, while when it exceeds 4 parts by weight, the hardening tends to become vigorous and the cost becomes undesirably expensive.

[0073] Another preferable embodiment of the invention is a rubber composition compounding 0.5-4 parts by weight of $N,N'-(4,4'\text{-diphenylmethane})$ bismaleimide and silica with 100 parts by weight of rubber ingredient containing not less than 50% by weight of at least one diene rubber of butadiene rubber and styrene-butadiene copolymer rubber.

[0074] When the compounding amount of $N,N'-(4,4'\text{-diphenylmethane})$ bismaleimide is less than 0.5 part by weight, the wet performances are not improved, while when it exceeds 4 parts by weight, the hardening of the rubber becomes vigorous and the cost becomes undesirably expensive.

[0075] Further, the dynamic storage modulus (E') of the rubber composition is preferable to be 7.0-16.0 MPa. When it is less than 7.0 MPa, the rigidity by feeling is insufficient, while when it exceeds 16.0 MPa, the ride comfort tends to be degraded. Similarly, the tensile stress at 300% elongation (M_{300}) is preferable to be 7.0-15.0 MPa. When it is less than 7.0 MPa, the rigidity by feeling is insufficient, while when it exceeds 15.0 MPa, the ride comfort tends to be degraded.

[0076] When the rubber composition according to the invention having the excellent properties as mentioned above is applied to a tread, since distribution of ground contact pressure of a tire can be uniformized, it largely contributes to the improvement of wet-skid performances.

[0077] In the pneumatic tire according to the invention, the above rubber composition is applied to the tread rubber. The structure of the tread is not particularly limited, and the rubber composition can be applied to one-layer structure comprising one tread rubber layer, a two-layer structure comprising cap rubber layer/base rubber layer, and further a multilayer structure. In any case, it is effective to arrange the rubber composition according to the invention at a ground contact side.

[0078] The rubber composition according to the invention is obtained by kneading the rubber ingredient, the maleimide compound, the nitrogen-containing compound, the reinforcing filler and the like described above by using a kneading machine such as rolls, internal mixer or the like, and vulcanizing after the forming. The rubber composition according to the invention can be suitably used in tire applications as a rubber member such as tire tread, under tread, carcass, sidewall, bead portion or the like as well as applications such as rubber vibration isolator, belt, hose and other industrial articles.

[0079] When the rubber composition according to the invention having the excellent properties as mentioned above is applied to a tread rubber of a pneumatic tire, since the distribution of ground contact pressure of the tire can be uniformized in addition to the aforementioned effects, the wet-skid performances are remarkably improved.

[EXAMPLE]

[0080] The invention will be described more concretely below.

(Physical properties of rubber composition)

[0081] Various compounding ingredients as shown in Tables 1 to 22 are kneaded and compounded with a laboratory plastomill of 500 ml and 3-inch rolls to obtain uncured rubber compositions, respectively. With respect to each rubber composition, a curelasto test and a blow point test are carried out by the following methods (1) and (2).

[0082] And also, the tensile test, dynamic viscoelasticity test and hardness measurement after the vulcanization of each rubber composition are carried out by the following methods (3) and (4).

(1) Curelasto test

[0083] The measurement is carried out at 145°C by using MDR2000 made by Flexis Inc. of U.S.A.

[0084] M_H and M_L are maximum and minimum values of torque, respectively, and T_{10} , T_{90} are times at which the rise of torque through vulcanization reaction reaches 10% and 90% of the total charge, respectively. Various data are represented by an index on the basis that Comparative Example 1 concerning the system compounded with carbon black as a filler, Comparative Example 3 concerning the system compounded with carbon black and silica as a filler, Comparative Example 6 concerning the system compounded with a large amount of silica as a filler and Comparative Example 8 concerning the system compounded with a large amount of carbon black as a filler are set to 100, respectively. As for the T_{10} and T_{90} , the nearer the indices to 100, the better the workability.

(2) Blow point test

[0085] Various data measured at 170°C under an activation energy of 20 kcal using a blow point measuring apparatus made by Toyo Seiki Co., Ltd. are represented by an index on the basis that Comparative Example 1 concerning the system compounded with carbon black as a filler, Comparative Example 3 concerning the system compounded with carbon black and silica as a filler, Comparative Example 6 concerning the system compounded with a large amount of silica as a filler and Comparative Example 8 concerning the system compounded with a large amount of carbon black as a filler are set to 100, respectively. The larger the index value, the larger the blow point value, and longer vulcanization time is required and hence the productivity is degraded.

(3) Tensile test

[0086] After vulcanization at 145°C for a period corresponding to 1.5 times the T_{90} obtained in the test (1), the tensile test is carried out according to JIS K 6301-1975 (using a No. 3 test piece) to measure an elongation at break (E_B), strength at break (T_B) and modulus at 300% elongation (M_{300}). Various data are represented by an index on the basis that Comparative Example 1 concerning the system compounded with carbon black as a filler, Comparative Example 3 concerning the system compounded with carbon black and silica as a filler, Comparative Example 6 concerning the system compounded with a large amount of silica as a filler and Comparative Example 8 concerning the system compounded with a large amount of carbon black as a filler are set to 100, respectively. The larger the index value, the better the fracture properties of the rubber composition.

(4) Dynamic viscoelasticity test

[0087] There are measured E' (dynamic storage modulus), E'' (dynamic loss modulus) and $\tan \delta$ (loss factor) at a frequency of 52 Hz, a measuring temperature of 30°C and a strain of 1 % by using a spectrometer (dynamic viscoelasticity measuring tester) made by Toyo Seiki Co., Ltd. Various data are represented by an index on the basis that Comparative Example 1 concerning the system compounded with carbon black as a filler, Comparative Example 3 concerning the system compounded with carbon black and silica as a filler, Comparative Example 6 concerning the system compounded with a large amount of silica as a filler and Comparative Example 8 concerning the system compounded with a large amount of carbon black as a filler are set to 100, respectively.

(5) Hardness

[0088] The measurement is conducted according to a hardness test (type A), JIS K6301-1975.

(Performances of a pneumatic tire)

[0089] Pneumatic tires of Embodiments 1 to 6 having a tire size of 185/70R14 and a tread of one-layer structure and pneumatic tires of Embodiment 7 having a tire size of 175/65R14 and a tread of one-layer structure are prepared according to conventional manner by using one of rubber compositions of Examples 2, 5, 7, 11, 12, 13, 14, 15, 19, 20, 21, 27, 28, 30, 31, 32, 33, 35, 37, 43, 44, 47, 49, 55, 56, 58, 59, 60, 61, 63, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 78, 81, 82, 84, 85, 86 and 87 and Comparative Examples 1, 3, 4, 6 and 8 as a tread rubber. The steering performance (maneuverability) on a wet road surface with respect to these tires is evaluated by an actual running test.

(1) Maneuverability on wet road surface

[0090] On a test course wetted by sprinkling water is actually run a vehicle of an FF 4-door sedan provided with each new tire, during which the driving performance, braking performance, steering responsibility and steering controllability are totally evaluated by a test driver while using the tire of Comparative Example 1, 6 or 8 as a control tire.

+1: a case that the professional test driver feels good to an extent of delicate recognition as compared to the control tire;

+2: a case that the professional test driver feels good to an extent of clear recognition as compared to the control tire;

+3: a case that a skilled driver among ordinary drivers feels good to an extent of recognition as compared to the control tire;

+4: a case that an ordinary driver feels good to an extent of recognition as compared to the control tire.

[0091] Further, the similar tire as mentioned above is prepared by using one of the rubber compositions of Examples 15, 19, 20, 21, 28, 32, 66, 71, 78, 81 and 82 and Comparative Examples 3, 4 and 6 as a tread rubber, and the performances of these tires are evaluated by a drum test according to the following method.

(2) Rolling resistance

[0092] After each tire is inflated under an internal pressure of 1.7 kg/cm², it is run on a large-size testing drum at a speed of 80 km/h for a given time under a load of 395 kg, and then run by inertia by cutting the driving force of the drum off, during which the rolling resistance is measured from the deceleration rate of the tire and represented by an index on the basis that the evaluated value in the tire of Comparative Example 1, 6 or 8 as a control tire is set to 100. The

larger the index value, the lower the rolling resistance and the better the result.

Embodiment 1:

- 5 **[0093]** In this embodiment, the effect of compounding a maleimide compound and the effect of further compounding a polyaniline are examined with respect to rubber compositions having a basic formulation of Table 1 and prepared according to Table 2 or Table 3. The results are shown in Table 2 and Table 3.

Table 1

	Parts by weight
Rubber ingredient * ¹	100
Carbon black * ²	Variable
Silica * ³	Variable
Silane coupling agent * ⁴	Variable
Aromatic oil	30
Stearic acid	2
Zinc white	3
Antioxidant * ⁵	1
Vulcanization accelerator * ⁶	Variable
Vulcanization accelerator * ⁷	1
Sulfur	1.75
Bismaleimide * ⁸	Variable
Polyaniline A, B, C or D * ⁹	Variable

*1: SBR1500 (Trademark: made by JSR Corporation)

*2: Seast 3H (Trademark: ISAF made by Tokai Carbon Co., Ltd.)

*3: Nipsil AQ (Trademark: made by Nippon Silica Kogyo Co., Ltd.)

*4: Si 69 (Trademark: made by Degussa AG of German)

*5: Noclac 6C (Trademark: made by Ohuchi Shinko Kagaku Kogyo Co., Ltd.)

*6: Nocceler D (Trademark: made by Ohuchi Shinko Kagaku Kogyo Co., Ltd.)

*7: Nocceler NS (Trademark: made by Ohuchi Shinko Kagaku Kogyo Co., Ltd.)

*8: N,N'-(4,4'-diphenylmethane) bismaleimide

*9A: ANILIX (Trademark: made by Mitsui Chemicals Fine, Inc.)

*9B: 4,4'-(m-phenylenediisopropylidene) dianiline

*9C: bis-3-aminophenyl sulphone

Table 2

(Compounding unit: parts by weight)													
	Batch No.	Comparative Example 1	Example 1	Example 2	Example 3	Comparative Example 2	Example 4	Example 5	Example 6	Example 7	Example 8	Example 9	Example 10
Formulation (ingredients in Table I, the amount of which is variable)	Carbon black ISAF	65.0	65.0	65.0	65.0	65.0	65.0	65.0	65.0	65.0	65.0	65.0	65.0
	Silica												
	Si 69	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
	Nocceler D	1.0	2.0	4.0			1.0	1.0	1.0	2.0	4.0	2.0	2.0
	Bismaleimide						0.5	1.0	2.0	1.0	2.0	1.0	
	Polyaniline A					2.0						1.0	
	Polyaniline B												1.0
	Polyaniline C												
Curelasto test	M _L	100	100	100	102	101	101	102	102	101	102	98	104
	M _H	100	110	115	123	99	113	115	120	121	128	119	125
	T ₁₀	100	103	107	115	85	99	95	89	99	95	102	89
	T ₉₀	100	125	149	163	90	110	102	96	112	108	115	98
Blow point test		100	131	156	188	99	101	97	92	102	99	103	95
Tensile test	EB	100.0	104.5	110.8	113.4	98.0	105.0	103.0	99.0	106.5	108.0	108.2	105.2
	TB	100.0	103.0	107.2	105.2	99.0	101.0	98.0	97.0	103.2	104.0	104.2	98.5
	M ₁₀₀	100.0	98.1	94.9	89.0	104.0	100.0	101.3	104.0	100.4	102.1	98.3	102.5
Dynamic visco-elasticity test	E'	100.0	125.6	133.9	145.0	105.0	130.5	134.5	142.3	140.2	156.3	139.7	143.5
	E''	100.0	122.1	118.4	125.0	115.5	126.0	117.0	122.4	122.4	133.4	123.7	121.0
	tan δ	100.0	97.2	88.4	86.2	110.0	96.5	87.0	86.0	87.3	85.3	88.5	84.3
Tire performances	Maneuverability	Control		+ 2				+ 2		+ 3			

Table 3

(Compounding unit: parts by weight)						
	Batch No.	Comparative Example 3	Example 11	Example 12	Example 13	Example 14
Formulation (ingredients in Table 1, the amount of which is variable)	Carbon black ISAF	35.0	35.0	35.0	35.0	35.0
	Silica	30.0	30.0	30.0	30.0	30.0
	Si 69	3.0	3.0	3.0	3.0	3.0
	Nocceler D	0.6	0.6	0.6	0.6	0.6
	Bismaleimide		2.0	1.0	2.0	2.0
	Polyaniline A			0.5	0.5	1.0
	Polyaniline B					
	Polyaniline C					
Curelasto test	M _L	100	100	100	102	103
	M _H	100	108	106	109	112
	T ₁₀	100	106	101	103	97
	T ₉₉	100	172	101	102	99
Blow point test		100	196	101	98	86
Tensile test	EB	100.0	103.9	98.0	99.0	97.2
	TB	100.0	94.6	96.0	94.2	95.6
	M ₃₀₀	100.0	93.1	102.0	104.0	105.6
Dynamic viscoelasticity test	E'	100.0	146.3	138.2	154.2	164.3
	E''	100.0	136.1	127.9	140.4	147.9
	tan δ	100.0	93.0	92.5	91.0	90.0
Tire performances	Maneuverability	Control	+2	+2	+3	+3

[0094] As seen from the above results, Comparative Example 2 using the polyaniline A alone is unfavorable because the blow point is similar to that of the control although T₉₀ is shortened and although E' raises slightly, tan δ considerably increases.

[0095] On the contrary, E' is increased by not less than 20% in Examples 1 to 3 using bismaleimide alone. Further, the delay of vulcanization is improved and the blow point is largely improved in Examples 4 to 10 using bismaleimide and polyaniline together. And also, E' largely rises and tan δ tends to lower as compared with the case using bismaleimide alone.

[0096] Furthermore, the similar synergistic effect is exhibited by using a bismaleimide and a polyaniline together even in the system using carbon black and silica together as shown in Comparative Example 3 and Examples 11 to 14.

[0097] According to this embodiment, there can be provided a rubber composition suitable for a tread rubber or the like having a high workability, a good productivity and a high modulus of elasticity. And also, a pneumatic tire using such a rubber composition in a tread is excellent in the maneuverability. Embodiment 2:

[0098] In this embodiment, the effect of compounding a maleimide compound and the effect of further compounding a hydrazide are examined with respect to rubber compositions having a basic formulation of Table 4 and prepared according to Table 5 to Table 7. The results are shown in Table 5 to Table 7.

Table 4

	Parts by weight
Rubber ingredient * ¹	100
Carbon black * ²	Variable
Silica * ³	Variable
Silane Coupling agent * ⁴	Variable
Aromatic Oil	30
Stearic acid	2
Zinc White	3
Antioxidant * ⁵	1
Vulcanization accelerator * ⁶	Variable
Vulcanization accelerator * ⁷	1
Sulfur	1.75
Bismaleimide * ⁸	Variable
Hydrazide A, B or C * ⁹	Variable

*1: SBR 1500 (Trademark: made by JSR Corporation)

*2: Seast 3H (Trademark: ISAF made by Tokai Carbon Co., Ltd.)

*3: Nipsil AQ (Trademark: made by Nippon Silica Kogyo Co., Ltd.)

*4: Si 69 (Trademark: made by Degussa AG of German)

*5: Noclac 6C (Trademark: made by Ohuchi Shinko Kagaku Kogyo Co., Ltd.)

*6: Nocceler D (Trademark: made by Ohuchi Shinko Kagaku Kogyo Co., Ltd.)

*7: Nocceler NS (Trademark: made by Ohuchi Shinko Kagaku Kogyo Co., Ltd.)

*8: N,N'-(4,4'-diphenylmethane) bismaleimide

*9A: 3-hydroxy, N'-(1,3-dimethylbutylidene)-2-naphthoic acid hydrazide

*9B: N'-(1,3-dimethylbutylidene)-salicylic acid hydrazide

*9C: isophthalic acid di(1,3-dimethylbutylidene) hydrazide

*9D: isonicotinic acid(1,3-dimethylbutylidene) hydrazide

Table 5

(Compounding unit: parts by weight)															
	Batch No.	Compar- ative Example 4	Example 15	Example 16	Example 17	Compar- ative Example 5	Example 18	Example 19	Example 20	Example 21	Example 22	Example 23	Example 24	Example 25	Example 26
Formulation (ingredients in Table 4, the amount of which is variable)	Carbon black	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0
	ISAF														
	Silica														
	Si 69														
	Nocceler D	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
	Bismaleimide		1.0	2.0	4.0		1.0	1.0	1.0	2.0	4.0	1.0	1.0	1.0	1.0
	Polyaniline A					1.0	0.25	0.5	1.0	0.5	1.0	0.5	1.0	0.5	0.5
Curelasto test	Polyaniline B														
	Polyaniline C														
	Polyaniline D														
	M _L	100	100	100	102	101	100	101	101	100	102	98	104	101	102
	M _H	100	110	115	123	100	113	117	123	121	131	119	125	112	114
Blow point test	T ₁₀	100	103	107	115	95	101	99	96	99	96	102	89	98	94
	T ₅₀	100	125	149	163	92	107	103	99	110	106	115	98	102	96
		100	131	156	188	102	105	98	97	101	99	103	95	97	95
		100.0	104.5	110.8	113.4	96.5	99.1	96.5	93.8	98.5	101.0	98.3	98.9	96.4	93.1
Tensile test	EB	100.0	103.0	107.2	105.2	99.0	101.0	98.0	97.3	97.5	100.4	99.5	102.0	98.9	99.5
	TB	100.0	98.1	94.9	89.0	105.0	100.0	103.5	105.7	105.2	105.8	101.5	104.2	103.4	106.2
	M ₁₀₀	100.0	125.6	133.9	145.0	102.0	130.3	135.2	142.3	141.3	155.4	132.5	138.5	130.2	136.2
Dynamic viscoelasticity test	E'	100.0	97.2	88.4	86.2	87.2	93.4	86.8	82.5	86.9	84.1	90.2	87.1	85.1	96.1
	tan δ	100.0													
Tire performances	Maneuver- ability	Control	+1					+2	+3	+3					
	Rolling resistance	100	100					103	105	103					

Table 6

(Compounding unit: parts by weight)						
	Batch No.	Comparative Example 3	Example 11	Example 27	Example 28	Example 29
Formulation (ingredients in Table 4, the amount of which is varia- ble)	Carbon black ISAF	35.0	35.0	35.0	35.0	35.0
	Silica	30.0	30.0	30.0	30.0	30.0
	Si 69	3.0	3.0	3.0	3.0	3.0
	Nocceler D	0.6	0.6	0.6	0.6	0.6
	Bismaleimide		2.0	1.0	2.0	2.0
	Hydrazide A			0.5	0.5	1.0
Curelasto test	M _L	100	100	100	102	103
	M _H	100	108	107	110	111
	T ₁₀	100	106	100	102	97
	T ₉₀	100	172	101	104	99
Blow point test		100	196	104	106	100
Tensile test	EB	100.0	103.9	96.5	95.6	96.5
	TB	100.0	94.6	99.5	100.6	99.8
	M ₃₀₀	100.0	93.1	99.8	97.3	98.7
	E'	100.0	146.3	138.2	156.2	168.2
	tan δ	100.0	93.0	87.5	86.5	82.1
Tire perform- ances	Maneuverability	Control	2	2	3	
	Rolling resist- ance	100			104	

Table 7

(Compounding unit: parts by weight)						
	Batch No.	Comparative Example 6	Example 30	Example 31	Example 32	Example 33
Formulation (ingredients in Table 4, the amount of which is varia- ble)	Carbon black ISAF	5.0	5.0	5.0	5.0	5.0
	Silica	60.0	60.0	60.0	60.0	60.0
	Si 69	6.0	6.0	6.0	6.0	6.0
	Nocceler D	0.9	0.9	0.9	0.9	0.9
	Bismaleimide		2.0	1.0	2.0	2.0
	Hydrazide A			0.5	0.5	1.0

Table 7 (continued)

(Compounding unit: parts by weight)						
	Batch No.	Comparative Example 6	Example 30	Example 31	Example 32	Example 33
Curelasto test	M _L	100	93	100	104	103
	M _H	100	97	100	102	103
	T ₁₀	100	106	102	104	105
	T ₉₀	100	158	98	98	100
Blow point test		100	178	108	105	102
Tensile test	EB	100.0	107.9	101.0	99.5	96.3
	TB	100.0	98.2	99.0	97.0	95.0
	M ₃₀₀	100.0	85.8	99.0	101.0	102.0
	E'	100.0	144.5	135.0	148.0	162.0
	tan δ	100.0	102.0	97.0	92.0	88.0
Tire performances	Maneuverability	Control	2	1	2	4
	Rolling resistance	100			103	

[0099] As seen from the above results, in Comparative Example 5 using hydrazide A alone, although T₉₀ is slightly short as compared to Comparative Example 1, the blow point is equal to that of the control and E' is not substantially increased.

[0100] On the contrary, in Examples 15 to 17 using bismaleimide alone, E' is increased by not less than 20%, and in Examples 18~26 using bismaleimide and hydrazide together, the delay of vulcanization is improved and the blow point is remarkably improved.

[0101] Furthermore, it can be seen that E' is considerably increased by compounding a hydrazide as compared with the case using bismaleimide alone and there is a synergistic effect by a combination of these two compounds.

[0102] Further, it can be seen that when the rubber compositions of Examples 19, 20, 21 are used in a tread, the wet maneuverability is improved and the rolling resistance value is decreased as compared to Comparative Example 4, whereby a higher maneuverability and a low fuel consumption can simultaneously be established.

[0103] Moreover, it can be seen that the similar synergistic effect is exhibited by using a bismaleimide and a hydrazide together even in the system using carbon black and silica together as shown in Comparative Example 3, Example 11 and Examples 27 to 29 and the system using a large amount of silica as shown in Comparative Example 6 and Examples 30 to 33.

[0104] According to this embodiment, there can be provided a rubber composition suitable as a tread rubber or the like having a high workability, a good productivity, a high elasticity and a low heat build-up. And also, a pneumatic tire using such a rubber in a tread is excellent in the maneuverability and low fuel consumption.

Embodiment 3:

[0105] In this embodiment, the effect of compounding a maleimide compound and the effect of further compounding a hydrazide of a type different from that of Embodiment 2 are examined with respect to rubber compositions having a basic formulation of Table 8 and prepared according to Table 9 or Table 10. The results are shown in Table 9 and Table 10.

Table 8

	Parts by weight
Rubber Ingredient * ¹	100
Carbon Black * ²	Variable
Silica * ³	Variable
Silane Coupling agent * ⁴	Variable
Aromatic Oil	30
Stearic acid	2
Zinc White	3
Antioxidant * ⁵	1
Vulcanization accelerator * ⁶	Variable
Vulcanization accelerator * ⁷	1
Sulfur	1.75
Bismaleimide * ⁸	Variable
Hydrazide E, F, G or H * ⁹	Variable

*1: SBR1500 (Trademark: made by JSR Corporation)

*2: Seast 3H (Trademark: made by Tokai Carbon Co., Ltd. ISAF)

*3: Nipsil AQ (Trademark: made by Nippon Silica Kogyo Co., Ltd.)

*4: Si 69 (Trademark: made by Degussa AG of German)

*5: Noclac 6C (Trademark: made by Ohuchi Shinko Kagaku Kogyo Co., Ltd.)

*6: Nocceler D (Trademark: made by Ohuchi Shinko Kagaku Kogyo Co., Ltd.)

*7: Nocceler NS (Trademark: made by Ohuchi Shinko Kagaku Kogyo Co., Ltd.)

*8: N,N'-(4,4'-diphenylmethane) bismaleimide

*9E: Adipic acid hydrazide

*9F: Salicylic acid hydrazide

*9G: Isophthalic acid hydrazide

*9H: 2-hydroxy-3-naphthoic acid hydrazide

Table 9

(Compounding unit: parts by weight)															
	Batch No.	Comparative Example 1	Example 1	Example 2	Example 3	Comparative Example 7	Example 34	Example 35	Example 36	Example 37	Example 38	Example 39	Example 40	Example 41	Example 42
Formulation (Ingredients in Table 8, the amount of which is variable)	Carbon black ISAF	65.0	65.0	65.0	65.0	65.0	65.0	65.0	65.0	65.0	65.0	65.0	65.0	65.0	65.0
	Silica Si 69														
	Nocceler D	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
	Bismaleimide		1.0	2.0	4.0		1.0	1.0	1.0	2.0	4.0	2.0	2.0	2.0	2.0
	Polyaniline E					1.0	0.25	0.5	1.0	0.5	1.0	0.5	1.0		
	Polyaniline F														
	Polyaniline G														
	Polyaniline H													0.5	0.5
Curelasto test	M _L	100	100	100	102	101	101	102	102	101	102	98	104	101	102
	M _H	100	110	115	123	99	112	115	120	121	128	119	125	116	117
	T ₁₀	100	103	107	115	94	101	99	96	99	96	102	89	98	94
	T ₉₀	100	125	149	163	90	108	102	98	111	108	115	98	102	96
Blow point test		100	131	156	188	98	103	97	92	97	99	103	95	96	91
Tensile test	EB	100.0	104.5	110.8	113.4	96.5	99.1	96.5	93.8	98.5	101.0	98.3	98.9	96.4	93.1
	TB	100.0	103.0	107.2	105.2	99.0	101.0	98.0	97.3	97.5	100.4	99.5	102.0	98.9	99.5
	M ₁₀₀	100.0	98.1	94.9	89.0	105.0	100.0	103.5	105.7	105.2	105.8	101.5	104.2	103.4	106.2
Dynamic viscoelasticity test	E'	100.0	125.6	133.9	145.0	102.0	128.2	133.2	138.5	141.3	155.4	139.7	143.5	135.6	137.9
	E''	100.0	122.1	118.4	125.0	100.5	122.3	122.7	122.7	122.8	130.7	115.4	114.0	115.4	111.0
	tan δ	100.0	97.2	88.4	86.2	98.5	95.4	92.1	88.6	86.9	84.1	82.6	79.4	85.1	80.5
Tire performances	Maneuverability	Control		+ 2				+ 2		+ 3					

Table 10

(Compounding unit: parts by weight)						
	Batch No.	Comparative Example 3	Example 11	Example 43	Example 44	Example 45
Formulation (ingredients in Table 8, the amount of which is variable)	Carbon black ISAF	35.0	35.0	35.0	35.0	35.0
	Silica	30.0	30.0	30.0	30.0	30.0
	Si 69	3.0	3.0	3.0	3.0	3.0
	Nocceler D	0.6	0.6	0.6	0.6	0.6
	Bismaleimide		2.0	1.0	2.0	2.0
	Hydrazide E			0.5	0.5	1.0
	Hydrazide F					
	Hydrazide G					
	Hydrazide H					
Curelasto test	M _L	100	100	100	102	103
	M _H	100	108	106	109	112
	T ₁₀	100	106	100	102	97
	T ₉₀	100	172	101	104	99
Blow point test		100	196	103	104	98
Tensile test	EB	100.0	103.9	96.5	95.6	96.5
	TB	100.0	94.6	99.5	100.6	99.8
	M ₃₀₀	100.0	93.1	103.4	102.5	106.8
Dynamic viscoelasticity test	E'	100.0	146.3	138.2	156.2	168.2
	E''	100.0	136.1	126.5	141.9	153.4
	tan δ	100.0	93.0	91.5	90.8	91.2
Tire performances	Maneuverability	Control	+2	+2	+2	

[0106] As seen from the above results, Comparative Example 7 is an example using hydrazide E alone, wherein although T₉₀ is shortened, the blow point is approximately equal to that of the control and E' hardly increases.

[0107] On the contrary, in Examples 34 to 40 using a bismaleimide and the hydrazide E together, the delay of vulcanization is improved and also the blow point is considerably improved, and E' increases and tan δ lowers as compared with Examples 1 to 3 using bismaleimide alone.

[0108] Further, it can be also understood that a similar synergistic effect is exhibited by simultaneously adopting a bismaleimide and a hydrazide, also in the blending system simultaneously adopting carbon black/silica as exhibited by Comparative Example 3, Example 11, and Examples 43 through 45.

[0109] According to this embodiment, there can be provided a rubber composition capable of improving a workability with a good productivity and having a higher elastic modulus and suitable for a tread rubber. Further, a pneumatic tire having a tread, for which such a rubber is utilized, has a superior maneuverability.

Embodiment 4:

[0110] In this embodiment, concerning the rubber compositions prepared according to the basic formulation of Table 11 and according to Table 12 through Table 14, there were considered a blending effect of the maleimide compound as well as an effect when an amine compound is simultaneously used. The results are shown in Table 12 through

Table 14.

Table 11

	Parts by Weight
Rubber Component * ¹	100
Carbon Black * ²	Variable
Silica * ³	Variable
Silane Coupling Agent * ⁴	Variable
Aroma Oil	30
Stearate	2
Zinc White	3
Antioxidant * ⁵	1
Vulcanization Accelerator * ⁶	Variable
Vulcanization Accelerator * ⁷	1
Sulfur	1.75
Bismaleimide * ⁸	Variable
Amine Compound A, B or C * ⁹	Variable

*1: SBR1500 (Trademark: manufactured by JSR Co., Ltd.)

*2: Seast (Trademark: ISAF manufactured by Tokai Carbon Co., Ltd.)

*3: Nipsil AQ (Trademark: manufactured by Nippon Silica Kogyo Co., Ltd.)

*4: Si69 (Trademark: manufactured by Degussa AG of German)

*5: Noclac 6C (Trademark: manufactured by Ohuchi Shinko Kagaku Kogyo Co., Ltd.)

*6: Nocceler D (Trademark: manufactured by Ohuchi Shinko Kagaku Kogyo Co., Ltd.)

*7: Nocceler NS (Trademark: manufactured by Ohuchi Shinko Kagaku Kogyo Co., Ltd.)

*8: N,N'-(4,4'-diphenylmethane)bismaleimide

*9A: dimethyl stearylamine/stearic acid salt

*9B: stearylamine/stearic acid salt

*9C: dimethyl stearylamine

Table 12

	Batch No.	Comparative Example 8	Example 15	Example 16	Example 17	Comparative Example 9	Example 46	Example 47	Example 48	Example 49	Example 50	Example 51	Example 52	Example 53	Example 54
Formulation (ingredients in Table 11, the amount of which is variable)	Carbon black ISAF	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0
	Silica	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
	Si 69	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
	Nocceler D		1.0	2.0	4.0		2.0	2.0	2.0	4.0	4.0	2.0	2.0	2.0	2.0
	Bismaleimide					2.0	1.00	2.0	4.0	2.0	4.0	2.0	2.0		
	Polyaniline A											2.0	4.0		
	Polyaniline B													1.0	2.0
	Polyaniline C														
Curelasto test	M _L	100	100	100	102	98	99	98	96	97	102	98	96	98	96
	M _H	100	110	115	123	103	109	111	123	115	131	111	123	111	123
	T ₁₀	100	103	107	115	95	101	99	96	99	96	99	96	99	96
	T ₉₀	100	125	149	163	93	107	105	96	109	106	106	97	103	95
Blow point test		100	131	156	188	96	105	101	95	97	99	102	95	101	95
Tensile test	M ₃₀₀	100.0	98.1	94.9	89.0	102.1	100.0	103.5	105.7	105.2	105.8	105.1	104.3	101.2	100.2
Dynamic viscoelasticity test	E'	100.0	125.6	133.9	145.0	101.2	133.6	135.2	136.8	141.3	148.1	135.9	136.5	137.2	138.1
	tan δ	100.0	97.2	88.4	86.2	97.2	88.3	87.5	87.1	86.9	85.2	88.1	87.1	85.2	84.1
Tire performances	Maneuverability	Control		+ 2				+ 2		+ 3					

(Compounding unit: parts by weight)

Table 13

(Compounding unit: parts by weight)						
	Batch No.	Comparative Example 3	Example 11	Example 55	Example 56	Example 57
Formulation (ingredients in Table 11, the amount of which is varia- ble)	ISAF Carbon Black	35.0	35.0	35.0	35.0	35.0
	Silica	30.0	30.0	30.0	30.0	30.0
	Si 69	3.0	3.0	3.0	3.0	3.0
	Nocceler D	0.6	0.6	0.6	0.6	0.6
	Bismaleimide		2.0	2.0	2.0	2.0
	Amine A			1.0	2.0	4.0
	Amine B					
	Amine C					
Curelasto test	M _L	100	100	97	92	87
	M _H	100	108	107	109	111
	T ₁₀	100	106	100	102	97
	T ₉₀	100	172	111	104	99
Blow point test		100	196	115	108	97
Tension Test	M ₃₀₀	100.0	93.1	99.8	99.9	101.2
Dynamic vis- coelasticity test	E'	100.0	146.3	148.2	149.3	151.2
	tan δ	100.0	93.0	89.1	86.5	83.5
Tire perform- ances	Maneuverability	Control	+2	+2	+3	

Table 14

(Compounding unit: parts by weight)						
	Batch No.	Comparative Example 6	Example 30	Example 58	Example 59	Example 60
Formulation (ingredients in Table 11, the amount of which is varia- ble)	ISAF Carbon Black	5.0	5.0	5.0	5.0	5.0
	Silica	60.0	60.0	60.0	60.0	60.0
	Si 69	6.0	6.0	6.0	6.0	6.0
	Nocceler D	0.9	0.9	0.9	0.9	0.9
	Bismaleimide		2.0	2.0	2.0	2.0
	Amine A			1.0	2.0	4.0
	Amine B					
	Amine C					

Table 14 (continued)

(Compounding unit: parts by weight)						
	Batch No.	Comparative Example 6	Example 30	Example 58	Example 59	Example 60
Curelasto test	M _L	100	93	89	87	81
	M _H	100	97	98	101	99
	T ₁₀	100	106	102	99	91
	T ₉₀	100	158	104	98	92
Blow point test		100	178	109	103	95
Tension test	M ₃₀₀	100.0	85.8	99.0	101.0	102.0
Dynamic viscoelasticity test	E'	100.0	144.5	143.1	142.5	143.2
	tan δ	100.0	102.0	98.0	96.0	92.0
Tire performance	Maneuverability	Control	+2	+1	+2	+4

[0111] From the above results, the amine addition salt itself tends to promote a vulcanization reaction in Comparative Example 9, but this is 10 % or less relative to Comparative Example 8 and is not a large effect.

[0112] Contrary, in Examples 46 through 54 simultaneously adopting a bismaleimide and an amine compound, the E' value is remarkably increased while substantially maintaining the M₃₀₀ value, so that not only the maneuverability on a wet road surface is improved, but also the delay of vulcanization is remarkably improved and the blow point is remarkably improved. Further, it can be understood that a similar synergistic effect is exhibited by simultaneously adopting a bismaleimide and an amine compound, in the systems including a large blending amount of silica as exhibited by Comparative Example 3, Example 11 and Examples 55 through 57.

[0113] According to this embodiment, there can be provided a rubber composition capable of improving a workability with a good productivity and having a higher elastic modulus and a lower heat build-up, which rubber composition is suitable for a tread rubber. Further, a pneumatic tire having a tread, for which such a rubber is utilized, has a superior maneuverability and rolling resistance.

Embodiment 5:

[0114] In this embodiment, concerning the rubber compositions prepared according to the basic formulation of Table 15 and according to Table 16 through Table 18, there was considered a blending effect when an oligomer or polymer of bismaleimide is used as a maleimide compound. The results are shown in Table 16 through Table 18.

Table 15

	Parts by Weight
Rubber Component * ¹	100
Carbon Black * ²	Variable
Silica * ³	Variable
Silane Coupling Agent * ⁴	Variable
Aroma Oil	30
Stearate	2
Zinc White	3
Antioxidant * ⁵	1
Vulcanization Accelerator * ⁶	Variable
Vulcanization Accelerator * ⁷	1
Sulfur	1.75
Maleimide Compound A, B or C * ⁸	Variable

*1: SBR1500 (Trademark: manufactured by JSR Co., Ltd.)

*2: Seast (Trademark: ISAF manufactured by Tokai Carbon Co., Ltd.)

*3: Nipsil AQ (Trademark: manufactured by Nippon Silica Kogyo Co., Ltd.)

*4: Si69 (Trademark: manufactured by Degussa AG of German)

*5: Nodac 6C (Trademark: manufactured by Ohuchi Shinko Kagaku Kogyo Co., Ltd.)

*6: Nocceler D (Trademark: manufactured by Ohuchi Shinko Kagaku Kogyo Co., Ltd.)

*7: Nocceler NS (Trademark: manufactured by Ohuchi Shinko Kagaku Kogyo Co., Ltd.)

*8A: Nocceler PM-P (Trademark: manufactured by Ohuchi Shinko Kagaku Kogyo Co., Ltd.)

*8B: Kelimid B601 (Trademark: manufactured by Asahi Chiba Co., Ltd.)

*8C: BT4680 (Trademark: manufactured by Mitsubishi Gas Chemical Co., Inc.)

Table 16

(Compounding unit: parts by weight)							
	Batch No.	Compara- tive Exam- ple 1	Example 61	Example 62	Example 63	Example 64	Example 65
Formulation (ingredients in Table 15, the amount of which is variable)	Carbon black ISAF	65.0	65.0	65.0	65.0	65.0	65.0
	Silica						
	Si 69						
	Nocceler D	0.3	0.3	0.3	0.3	0.3	0.3
	Maleimide compound A		2.0				
	Maleimide compound B			1.0	2.0	3.0	
	Maleimide compound C						2.0
Curelasto test	M _L	100	100	101	102	102	102
	M _H	100	115	111	115	120	113
	T ₁₀	100	107	104	107	106	105
	T ₉₀	100	149	98	102	104	106
Blow point test		100	156	99	97	96	101
Tension test	E _B	100.0	110.8	102.0	103.0	99.0	105
	T _B	100.0	107.2	101.0	98.0	97.0	102
	M ₃₀₀	100.0	94.9	100.0	100.8	102.0	98.0
Dynamic vis- coelasticity test	E'	100.0	133.9	116.0	130.0	144.0	132.0
	tan δ	100.0	88.4	95.0	87.0	86.0	95.1
Tire perform- ance	Maneuvera- bility	Control	+2	Not exer- cised	+2	Not exer- cised	+2

Table 17

(Compounding Unit: parts by weight)							
	Batch No.	Compara- tive Exam- ple 3	Example 66	Example 67	Example 68	Example 69	Example 70
Formulation (ingredients in Table 15, the amount of which is variable)	Carbon Black ISAF	35.0	35.0	35.0	35.0	35.0	35.0
	Silica	30.0	30.0	30.0	30.0	30.0	30.0
	Si 69	3.0	3.0	3.0	3.0	3.0	3.0
	Nocceler D	0.6	0.6	0.6	0.6	0.6	0.6
	Maleimide compound A		2.0				
	Maleimide compound B			1.0	2.0	3.0	
	Maleimide compound C						2.0
Curelasto test	M _L	100	100	100	104	102	103
	M _H	100	108	106	107	105	106
	T ₁₀	100	106	103	103	105	105
	T ₉₀	100	171	102	105	108	107
Blow point test		100	196	103	95	86	101
Tension Test	E _B	100.0	103.9	98.0	99.0	97.2	102
	T _B	100.0	94.6	96.0	94.2	95.6	100
	M ₃₀₀	100.0	93.1	102.0	104.0	106.0	96.2
Dynamic vis- coelasticity test	E'	100.0	137.0	124.0	144.0	158.0	142.1
	tan δ	100.0	105.0	95.0	91.0	90.0	96.5
Tire perform- ance	Maneuvera- bility	Control	+2	+1	+2	+3	+2

Table 18

(Compounding unit: parts by weight)							
	Batch No.	Compara- tive Exam- ple 6	Example 71	Example 72	Example 73	Example 74	Example 75
Formulation (Ingredients in Table 15, the amount of which is variable)	Carbon Black ISAF	5.0	5.0	5.0	5.0	5.0	5.0
	Silica	60.0	60.0	60.0	60.0	60.0	60.0
	Si 69	6.0	6.0	6.0	6.0	6.0	6.0
	Nocceler D	0.9	0.9	0.9	0.9	0.9	0.9
	Maleimide compound A		2.0				
	Maleimide compound B			1.0	2.0	3.0	
	Maleimide compound C						2.0
Curelasto test	M _L	100	93	100	104	103	103
	M _H	100	97	99	101	102	102
	T ₁₀	100	106	102	104	105	108
	T ₉₀	100	158	96	98	100	103
Blow point test		100	178	105	104	101	108
Tension test	E _B	100.0	107.9	101.0	99.5	96.3	105
	T _B	100.0	98.2	99.0	97.0	95.0	102
	M ₃₀₀	100.0	85.8	98.0	102.0	103.0	87.9
Dynamic vis- coelasticity Test	E'	100.0	139.0	120.0	146.0	160.0	143.2
	tan δ	100.0	108.0	101.0	99.0	97.0	101.8
Tire perform- ance	Maneuvera- bility	Control	+3	+1	+3	+4	+3

[0115] From the above results, when 2.0 parts by weight of bismaleimide is blended into Comparative Example 1 (i.e., in Example 61), E' is increased by 30 % or more, and the tire performance is also remarkably improved. Further, by adopting an oligomer or polymer of bismaleimide, E' is remarkably increased similarly to the situation adopting a bismaleimide, while T₉₀ and blow point value are not so affected that the productivity is not deteriorated.

[0116] Further, when these rubber compositions were used as a tire tread, there was obtained a higher maneuverability of tire substantially identical with the case of bismaleimide.

[0117] Substantially same effects were also confirmed in the systems simultaneously adopting carbon black and silica as exhibited by Comparative Example 3 and Examples 66 through 70, and in the systems adopting a large amount of silica as exhibited by Comparative Example 6 and Examples 71 through 75.

[0118] According to this embodiment, there can be provided a rubber composition capable of improving a workability with a good productivity and having a higher elastic modulus and suitable for a tread rubber. Further, a pneumatic tire having a tread, for which such a rubber is utilized, has a superior maneuverability.

Embodiment 6:

[0119] In this embodiment, concerning the rubber compositions prepared according to the basic formulation of Table 19 and according to Table 20 or Table 21, there was considered a blending effect of various maleimide compounds. The results are shown in Table 20 and Table 21.

Table 19

	Parts by Weight
Rubber Component *1	100
Carbon Black *2	Variable
Silica *3	Variable
Silane Coupling Agent *4	Variable
Aroma Oil	30
Stearate	2
Zinc White	3
Antioxidant *5	1
Vulcanization Accelerator *6	Variable
Vulcanization Accelerator *7	1
Sulfur	1.75
Maleimide Compound D, E, F, C or H *8	Variable

*1: SBR1500 (Trademark: manufactured by JSR Co., Ltd.)

*2: Seast (Trademark: ISAF manufactured by Tokai Carbon Co., Ltd.)

*3: Nipsil AQ (Trademark: manufactured by Nippon Silica Kogyo Co., Ltd.)

*4: Si69 (Trademark: manufactured by Degussa AG of German)

*5: Noclac 6C (Trademark: manufactured by Ohuchi Shinko Kagaku Kogyo Co., Ltd.)

*6: Nocceler D (Trademark: manufactured by Ohuchi Shinko Kagaku Kogyo Co., Ltd.)

*7: Nocceler NS (Trademark: manufactured by Ohuchi Shinko Kagaku Kogyo Co., Ltd.)

*8D: N,N'-(1,3-phenylene)bismaleimide

*8E: 1,3-bis(citraconimide) benzene

*8F: 1,3-bis(citraconimidemethyl) benzene

*8G: N-phenyl maleimide

*8H: N-methyl maleimide

*8I: N,N'-(4,4'-diphenylmethane)bismaleimide

Table 20

	Batch No.	Comparative Example 3	(Compounding unit: parts by weight)									
			Example 66	Example 76	Example 77	Example 78	Example 79	Example 80	Example 81	Example 82		
Formulation (ingredients in Table 19, the amount of which is variable)	Carbon black ISAF	35.0	35.0	35.0	35.0	35.0	35.0	35.0	35.0	35.0		
	Silica	30.0	30.0	30.0	30.0	30.0	30.0	30.0	30.0	30.0		
	Si 69	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0		
	Nocceler D	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6		
	Maleimide compound D	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0		
	Maleimide compound E											
	Maleimide compound F											
	Maleimide compound G											
	Maleimide compound H											
	Maleimide compound I											
Tensile test	M ₃₀₀	100.0	94.9	96	91	75	87	98	96	95		
Dynamic viscoelasticity test	E'	100.0	137.0	127.4	116.4	136.2	123.2	124.0	136.0	148.0		
	tan δ	100.0	105.0	114.7	118.6	114.4	115.9	98.0	97.5	98.0		
Tire performances	Rolling resistance	100	97			94			101	102		
	Maneuverability	Control	2			2			2	3		

Table 21

(Compounding unit: parts by weight)						
	Batch No.	Comparative Example 6	Example 71	Example 83	Example 84	Example 85
Formulation (ingredients in Table 19, the amount of which is variable)	Carbon black ISAF	5.0	5.0	5.0	5.0	5.0
	Silica	60.0	60.0	60.0	60.0	60.0
	Si69	6.0	6.0	6.0	6.0	6.0
	Nocceler D	0.9	0.9	0.9	0.9	0.9
	Maleimide compound A		2.0			
	Maleimide compound I			1.0	2.0	3.0
Tension test	M ₃₀₀	100.0	89.0	95	93	89
Dynamic viscoelasticity test	E'	100.0	139.0	122.0	137.0	149.0
	tan δ	100.0	108.0	100.0	99.0	101.0
Tire performance	Rolling Resistance	100	94		100	100
	Maneuverability	Control	2		2	3

Maleimide Compound I: 1,3-phenylene bismaleimide

[0120] As seen from the above results, M₃₀₀ is decreased and E' is largely increased to improve the maneuverability of tire by using a maleimide compound. Particularly, in case of using N,N'-(methylene-di-p-phenylene) bismaleimide as shown in Examples 80, 81 and 82, E' increases to improve the maneuverability of the tire but also tan δ at 60°C becomes smaller than that of the control (Comparative Example 3) and the rolling resistance of the tire becomes substantially equal to the control.

[0121] It can be seen that even in the system using a large amount of silica as shown in Comparative Example 6, Example 71 and Examples 83 to 85, the maneuverability of the tire and rolling resistance of the tire can simultaneously be established at a higher level, which has never been attained in the conventional technique, by compounding bismaleimide, particularly N,N'-(4,4'-diphenylmethane) bismaleimide.

Embodiment 7:

[0122] In this embodiment, the compounding effect using 1,3-phenylene bismaleimide as a maleimide compound is examined with respect to rubber compositions prepared according to the formulation of Table 22. The results are shown in Table 22.

Table 22

(Compounding unit: parts by weight)		
	Comparative Example 10	Example 86
E-SBR	100	100
ZrO	5	5
Stearic acid	3	3
Silica	50	50

Table 22 (continued)

(Compounding unit: parts by weight)		
	Comparative Example 10	Example 86
Process oil	3	3
Vulcanization accelerator/S	0.8/2.2	0.8/2.2
Maleimide compound I	0	2
Hardness	68	68
E' (MPa)	11.3	15.5
M ₃₀₀ (MPa)	7.65	7.31
Maneuverability	Control	+3
Vulcanization accelerator: N-oxydiethylene-2-benzothiazyl sulfeneamide		

E-BSR: (SBR1500: Trademark: made by JSR Corporation)

Maleimide compound I: 1,3-phenylene bismaleimide

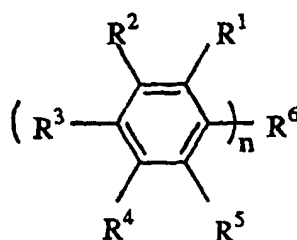
[0123] As seen from the test results, the balance between E' and M₃₀₀ (large deformation modulus) can be optimized in Example 86, and particularly, distribution of ground contact pressure of a tire on a wet road surface having a low frictional coefficient is uniformized to improve maneuvering performance on a wet road surface.

[0124] As mentioned above, according to the invention, there can be provided a rubber composition capable of improving maneuverability on a slippery wet road surface having an extremely low frictional coefficient and having a low rolling resistance without exerting upon the productivity of tire and other performances.

Claims

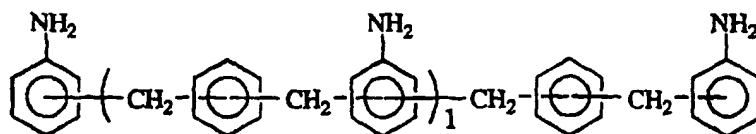
1. A rubber composition comprising at least one of natural rubber and synthetic diene rubbers as a rubber ingredient, at least one maleimide compound and at least one nitrogen-containing compound selected from the group consisting of polyaniline, hydrazide and amine compound.

2. A rubber composition according to claim 1, wherein the polyaniline is represented by the following general formula [1]:



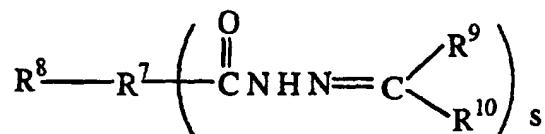
(wherein R¹, R², R³, R⁴ and R⁵ each independently represents H or NH₂, at least one of R¹-R⁵ is NH₂, n is an integer of not less than 2, R⁶ is n-valent hydrocarbon residue, -O-, -S- or -SO₂- provided that the hydrocarbon residue may be saturated, unsaturated, aliphatic, aromatic, branched or straight chain and may include at least one hetero atom).

3. A rubber composition according to claim 2, wherein the polyaniline is bis(3-aminophenyl) sulphone, 4,4'-(m-phenylene diisopropylidene) dianiline, or an aromatic polyaniline represented by the following general formula [2]:

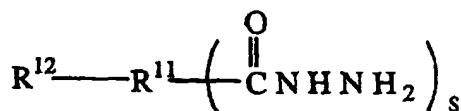


(wherein 1 is an integer of not less than 0).

4. A rubber composition according to claim 1, wherein the hydrazide is represented by the following general formula [3] or [4]:



(wherein R^7 is a non-cyclic aliphatic group having a carbon number of 2-18, a cyclic aliphatic group having a carbon number of 5-20, an aromatic group having a carbon number of 6-18 or an alkyl aromatic group having a carbon number of 7-24 and may include at least one hetero atom of O, N and S, provided that the non-cyclic aliphatic group may include an aromatic group therein, R^8 is a hydrogen atom, a hydroxy group, an amino group or a mercapto group, R^9 and R^{10} are a hydrogen atom, an alkyl group having a carbon number of 1-18, a cyclohexyl group or an aromatic group and may include at least one hetero atom of O, N and S and are the same or different, and s is an integer of 1-3);

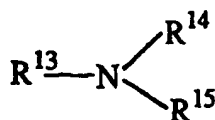


(wherein R^{11} is a non-cyclic aliphatic group having a carbon number of 2-18, a cyclic aliphatic group having a carbon number of 5-20, an aromatic group having a carbon number of 6-18 or an alkyl aromatic group having a carbon number of 7-24 and may include at least one hetero atom of O, N and S, provided that the non-cyclic aliphatic group may include an aromatic group therein, R^{12} is a hydroxy group, an amino group, a hydrazide group or a mercapto group; and s is an integer of 1-3).

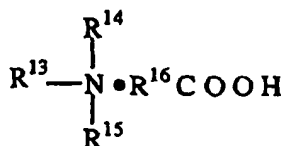
5. A rubber composition according to claim 4, wherein the hydrazide is 1-hydroxy, N'-(1-methylethylidene)-2-naphthoic acid hydrazide, 1-hydroxy, N'-(1-methylpropylidene)-2-naphthoic acid hydrazide, 1-hydroxy, N'-(1-methylbutylidene)-2-naphthoic acid hydrazide, 1-hydroxy, N'-(1,3-dimethylbutylidene)-2-naphthoic acid hydrazide, 1-hydroxy, N'-(2,6-dimethyl-4-heptylidene)-2-naphthoic acid hydrazide, 1-hydroxy, N'-(2-furylmethylene)-2-naphthoic acid hydrazide, 3-hydroxy, N'-(1-methylethylidene)-2-naphthoic acid hydrazide, 3-hydroxy, N'-(1-methylpropylidene)-2-naphthoic acid hydrazide, 3-hydroxy, N'-(1-methylbutylidene)-2-naphthoic acid hydrazide, 3-hydroxy, N'-(1,3-dimethylbutylidene)-2-naphthoic acid hydrazide, 2-hydroxy, N'-(2,6-dimethyl-4-heptylidene)-3-naphthoic acid hydrazide, 2-hydroxy, N'-(2-furylmethylene)-3-naphthoic acid hydrazide, isophthalic acid di(1-methylethylidene) hydrazide, isophthalic acid di(1-methylpropylidene) hydrazide, isophthalic acid di(1-methylbutylidene) hydrazide, isophthalic acid di(1,3-dimethylbutylidene) hydrazide, isophthalic acid di(2,6-dimethyl-4-heptylidene) hydrazide, isophthalic acid di(2-furylmethylene) hydrazide, isonicotinic acid (1-methylethylidene) hydrazide, isonicotinic acid (1-methylpropylidene) hydrazide, isonicotinic acid (1-methylbutylidene) hydrazide, isonicotinic acid (2,6-dimethyl-4-heptylidene) hydrazide, isonicotinic acid (1,3-dimethylbutylidene) hydrazide, isonicotinic acid (2-furylmethylene) hydrazide, N'-(1-methylethylidene)-salicylic acid hydrazide, N'-(1-methylpropylidene)-salicylic acid hydrazide, N'-(1-methylbutylidene)-salicylic acid hydrazide, N'-(1,3-dimethylbutylidene)-salicylic acid hydrazide, N'-(2,6-dimethyl-4-heptylidene)-salicylic acid hydrazide, N'-(2-furylmethylene)-salicylic acid hydrazide, adipic acid dihydrazide, iso-

phthalic acid dihydrazide, salicylic acid hydrazide or 2-hydroxy-3-naphthoic acid hydrazide.

6. A rubber composition according to claim 1, wherein the amine is at least one amine compound comprising an amine represented by the following general formula [5] and an amine addition salt represented by the following general formula [6]:

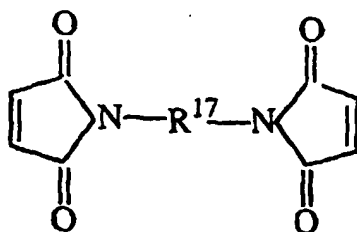


(wherein R^{13} is a saturated or an unsaturated alkyl group having a carbon number of 8-24, an aryl group having a carbon number of 6-24 or an aralkyl group having a carbon number of 7-24, R^{14} and R^{15} are a hydrogen atom, a saturated or an unsaturated alkyl group having a carbon number of 1-12, an aryl group having a carbon number of 6-12, an aralkyl group having a carbon number of 7-12, $-(\text{CH}_2\text{O})_p\text{H}$, $-(\text{CH}_2\text{CH}_2\text{O})_p\text{H}$, $-(\text{CH}(\text{CH}_3)\text{CH}_2\text{O})_p\text{H}$ or $-(\text{CH}_2\text{CH}_2\text{CH}_2\text{O})_p\text{H}$, respectively, provided that a total value of p in R^{14} and R^{15} is an integer of 1-4);



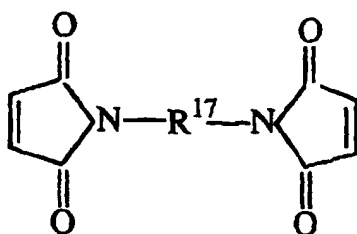
(wherein R^{13} - R^{15} are the same as defined above and R^{16} is a saturated or an unsaturated alkyl group having a carbon number of 6-24, an aryl group having a carbon number of 6-24 or an aralkyl group having a carbon number of 7-24).

7. A rubber composition according to claim 6, wherein in the general formulae of the amine and the amine addition salt, R^{14} and R^{15} independently are a saturated or an unsaturated alkyl groups having a carbon number of 1-8, and a total value of the carbon number in R^{13} , R^{14} and R^{15} in each of the amine and the amine addition salt is 10-24.
8. A rubber composition according to claim 6, wherein the amine is dimethyl stearylamine or stearylamine.
9. A rubber composition according to claim 6, wherein the amine addition salt is a stearic acid salt of dimethyl stearylamine or a stearic acid salt of methyl stearylamine.
10. A rubber composition according to claim 1, wherein the maleimide compound is a bismaleimide compound, or an oligomer or polymer of maleimide.
11. A rubber composition according to claim 10, wherein the oligomer or polymer of maleimide is an oligomer or polymer of bismaleimide.
12. A rubber composition comprising at least one of natural rubber and synthetic diene rubbers as a rubber ingredient and at least one maleimide compound selected from the group consisting of bismaleimide, oligomer and polymer of bismaleimide.
13. A rubber composition according to claim 10, wherein the bismaleimide compound is at least one compound represented by the following general formula [7]:



(wherein R^{17} is R^{18} or R^{19} - R^{18} - R^{20} , R^{18} is an aromatic group having a carbon number of 6-18, an alkyl aromatic group having a carbon number of 7-24 or a methylene group, and R^{19} and R^{20} are an alkylene group having a carbon number of 1-3 or a phenylene group, respectively).

14. A rubber composition according to claim 12, wherein the bismaleimide compound is at least one compound represented by the following general formula [7]:



(wherein R^{17} is R^{18} or R^{19} - R^{18} - R^{20} , R^{18} is an aromatic group having a carbon number of 6-18, an alkyl aromatic group having a carbon number of 7-24 or a methylene group, and R^{19} and R^{20} are an alkylene group having a carbon number of 1-3 or a phenylene group, respectively).

15. A rubber composition according to claim 13, wherein the bismaleimide compound is at least one selected from the group consisting of N,N'-(4,4'-diphenylmethane) bismaleimide and N,N'-(1,3-phenylene) bismaleimide.
16. A rubber composition according to claim 14, wherein the oligomer or polymer of a bismaleimide is at least one of a polyamino bismaleimide resin and a bismaleimide triazine resin.
17. A rubber composition according to claim 1, further comprising at least one filler selected from the group consisting of carbon black and silica.
18. A rubber composition according to claim 1, further comprising at least one vulcanization accelerator selected from the group consisting of thiazoles, thiurams and dithiocarbamates.
19. A rubber composition according to claim 1, wherein the rubber ingredient contains not less than 50% by weight of at least one selected from the group consisting of styrene-butadiene copolymer rubber and butadiene rubber.
20. A rubber composition according to any one of claims 1 to 17, wherein the rubber ingredient contains not less than 50% by weight of styrene-butadiene copolymer rubber.
21. A rubber composition according to claim 19, wherein the styrene-butadiene copolymer rubber is obtained by emulsion polymerization.
22. A rubber composition according to claim 1, wherein the maleimide compound is compounded in an amount of 0.1-30 parts by weight per 100 parts by weight of the rubber ingredient.
23. A rubber composition according to claim 1, wherein the polyaniline is compounded at a ratio of 10-200% by weight of the maleimide compound.

24. A rubber composition according to claim 1, wherein the hydrazide is compounded at a ratio of 5-200% by weight of the maleimide compound.

5 25. A rubber composition according to claim 1, wherein the amine compound is compounded at a ratio of 50-400% by weight of the maleimide compound.

26. A rubber composition according to claim 1, wherein a dynamic storage modulus (E') is 7.0-16.0 MPa, and a tensile stress at 300% elongation (M_{300}) is 7.0-15.0 MPa.

10 27. A pneumatic tire comprising a tread portion, wherein a rubber composition comprising at least one of natural rubber and synthetic diene rubbers as a rubber ingredient, at least one maleimide compound, and at least one nitrogen-containing compound selected from the group consisting of polyaniline, hydrazide and amine compound is used as a rubber composition constituting the tread portion.

15 28. A pneumatic tire comprising a tread portion, wherein a rubber composition comprising at least one of natural rubber and synthetic diene rubbers as a rubber ingredient, at least one maleimide compound selected from the group consisting of bismaleimide, oligomer and polymer of bismaleimide.

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP00/00659

A. CLASSIFICATION OF SUBJECT MATTER		
Int. Cl. ⁷ C08L7/00, C08L9/00, C08K5/3415, C08K5/18, C08K5/24, C08K5/17, B60C1/00		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols)		
Int. Cl. ⁷ C08L7/00, C08L9/00, C08K5/3415, C08K5/18, C08K5/24, C08K5/17, B60C1/00		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP, 564966, A2 (The Goodyear Tire & Rubber Company), 13 October, 1993 (13.10.93), Claims; page 6, lines 15 to 19	1-26
Y	Claims; page 6, lines 15 to 19 & JP, 06-025308, A Claims; Par. No. 0021 & US, 5616279, A & US, 5736615, A & CA, 2076056, A	1-28
X	EP, 570825, A1 (The Goodyear Tire & Rubber Company), 24 November, 1993 (24.11.93), Claims; page 6, lines 48 to 51	1-28
Y	Claims; page 6, lines 48 to 51 & JP, 06-136184, A Claims; page 9, left column, lines 19 to 25 & US, 5244028, A & BR, 9301917, A & CA, 2078403, A & DE, 69303922, C3	1-28
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 08 May, 2000 (08.05.00)		Date of mailing of the international search report 16 May, 2000 (16.05.00)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
Facsimile No.		Telephone No.

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP00/00659

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP, 60-245652, A (Sumitomo Chemical Company, Limited), 05 December, 1985 (05.12.85), Claims	1-26
Y	Claims (Family: none)	1-28
Y	JP, 63-099251, A (Bridgestone Corporation), 30 April, 1988 (30.04.88), Claims (Family: none)	1-28
Y	JP, 10-139934, A (Bridgestone Corporation), 26 May, 1998 (26.05.98), Claims (Family: none)	1-28

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